

Multiple Time-Scale Behaviour and Network Dynamics in Liquid Methanol

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Abstract

Canonical ensemble molecular dynamics simulations of liquid methanol, modeled using a rigid-body, pair-additive potential, are used to compute static distributions and temporal correlations of tagged molecule potential energies as a means of characterising the liquid state dynamics. The static distribution of tagged molecule potential energies shows a clear multimodal structure with three distinct peaks, similar to those observed previously in water and liquid silica. The multimodality is shown to originate from electrostatic effects, but not from local, hydrogen-bond interactions. An interesting outcome of this study is the remarkable similarity in the tagged potential energy power spectra of methanol, water and silica, despite the differences in the underlying interactions and the dimensionality of the network. All three liquids show a distinct multiple time scale (MTS) regime with a $1/f^\alpha$ dependence with a clear positive correlation between the scaling exponent α and the diffusivity. The low-frequency limit of the MTS regime is determined by the frequency of crossover to white noise behaviour which occurs at approximately 0.1 cm^{-1} in the case of methanol under standard temperature and pressure conditions. The power spectral regime above 200 cm^{-1} in all three systems is dominated by resonances due to localised vibrations, such as librations. The correlation between α and the diffusivity in all three liquids appears to be related to the strength of the coupling between the localised motions and the larger length/time-scale network reorganizations. Thus the time scales associated with network reorganization dynamics appear to be qualitatively similar in these systems, despite the fact that water and silica both display diffusional anomalies but methanol does not.

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1 Introduction

Considerable experimental as well as theoretical attention has been devoted to characterizing the structure and dynamics of hydrogen-bonded liquids [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. The motivation for these studies is primarily due to the importance of water as a solvent for biological and chemical processes. A comparison of the behaviour of water with other second-row hydrides, such as HF, NH₃ and CH₃OH, is essential for understanding the nature of hydrogen-bonded dynamics and the extent to which the behaviour of water is unique. Methanol, in particular, is of interest because it is the simplest molecule which can exhibit both hydrogen bonding and nonpolar interactions.

While interactions in simple liquids are dominated by steep, short-range repulsions and long-range, isotropic attractions, hydrogen-bonded liquids have strong, local anisotropic interactions. In the case of water, each molecule can form at most four hydrogen bonds, leading to a three-dimensional, open, locally tetrahedral network structure. The strength of hydrogen bonds is estimated to lie between 5 and 10k_BT at melting [11] which is strong enough that a substantial fraction of hydrogen bonds will be intact at room temperature. Thermal fluctuations will, however, be large enough, in comparison to the bond strength, to ensure that such bonds will have a finite lifetime of the order of picoseconds. As a result, the dynamics of the liquid will be dominated by the behaviour of the three-dimensional, hydrogen-bonded network, parts of which are constantly broken and reformed. In the case of methanol, hydrogen bond strengths are similar to those in water [12], but each methanol molecule can form at most three hydrogen bonds, of which only one can be as a proton donor. In liquid methanol, however, simulations as well as neutron scattering experiments show that the typical number of hydrogen bonds per molecule is two [13, 14, 15]. Consequently, linear chains with very rare branch points are seen, rather than the three-dimensional network characteristic of water.

Hydrogen-bonded liquids can be thought of as a subset of network-forming liquids, other examples being ionic melts such as ZnCl₂, SiO₂ and BeF₂ [16]. The strong local coupling of individual atomic or molecular units leads to the existence of multiple length and time scales corresponding to cooperative rearrangements of the network involving different numbers of molecules. To characterise the dynamical behaviour of network-forming liquids, it is convenient to use the power spectral density of a mechanical quantity that is sensitive to motion on a number of different length scales. The power spectral density of an observable $A(t)$ as a function of time t over a time interval T , is defined as[17]

$$S(f) = \lim_{T \rightarrow \infty} \frac{1}{T} \left| \int_{-T/2}^{T/2} A(t) e^{2\pi i f t} dt \right|^2. \quad (1)$$

where $S(f)$ is the spectral power associated with frequency f . In a recent set of studies, we have shown that the power spectrum associated with the tagged particle potential energy can be used

to characterize the dynamics of tetrahedral, network-forming liquids, such as water [18, 19, 20, 21, 22] and SiO_2 [23]. Simple liquids show a white noise power spectrum where $S(f)$ is independent of frequency. Network-forming liquids, however, have a characteristic multiple time-scale regime with $1/f^\alpha$ dependence on frequency f with α lying between 1 and 1.8 [24]. The three liquids that we have studied all show a region of anomalous diffusivity where mobility increases on isothermal compression; this density-dependent variation in mobility is strongly correlated with the scaling exponent α . Our results therefore suggest that monitoring the power spectrum of tagged particle potential fluctuations to be a simple and direct method for linking phenomena on three distinctive length and time scales: the local molecular environment, hydrogen bond network reorganisations and the diffusivity.

In this work, we characterise the multiple time-scale behaviour of liquid methanol, focusing primarily on the power spectrum of the tagged particle potential energy. Methanol presents an interesting contrast to the systems we have studied earlier since hydrogen bonding results in formation of one-dimensional chains, rather than a three-dimensional network. Unlike water, methanol does not show any anomalous liquid state properties, such as the diffusional anomaly mentioned above, or thermodynamic anomalies related to the existence of a temperature of maximum density under isobaric conditions. It is therefore interesting to compare the manner in which the multiple time-scale behaviour of methanol and water differ. We perform molecular dynamics simulations of methanol using Haughney's H1 potential [25] which predicts thermodynamic, structural and transport properties in fair agreement with a wide variety of experimental data[13, 14, 26, 27, 28] as well as recent ab initio molecular dynamics simulations [29, 30]. Section 2 contains details of the molecular dynamics simulations as well as of the power spectral analysis. Section 3 contains a discussion of our results, and Section 4 presents the conclusions.

2 Computational Details

2.1 Potential energy surface

The intermolecular interactions in methanol are modeled using Haughney's H1 pair-potential which treats methanol as a rigid three-site entity where the centres of interaction are positioned on the carbon (C), oxygen (O) and the hydroxyl proton H_O [25]. The interaction between any two methanol molecules α and β has the following functional form:

$$U_{\alpha\beta} = \sum_i \sum_j 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (2)$$

where the indices i and j label the atomic sites on the two molecules and r_{ij} corresponds to the site-site separation. The atomic sites are labelled by the partial charge, and the Lennard-Jones parameters σ_{ii}

and ϵ_{ii} , which are summarised in Table I. The Lennard-Jones parameters for interactions between unlike atoms are obtained using the Lorentz-Berthelot mixing rules: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. The molecular geometry is specified using the following bond lengths and bond angles: $r(\text{C-O})=1.4246\text{\AA}$, $r(\text{O-H}_O)= 0.9451\text{\AA}$, $r(\text{C-H})=1.0936\text{\AA}$, $\angle \text{COH}_O = 108.53^\circ$ and $\angle \text{HCH} = 108.63^\circ$. The methyl protons are not considered as interaction sites but they are included when specifying the molecular geometry, so that the molecules have correct masses and moments of inertia.

2.2 Molecular Dynamics

Molecular Dynamics (MD) simulations of a system of 256 methanol molecules were carried out in canonical (NVT) ensemble, using the DL_POLY software package [31, 32], under cubic periodic boundary conditions. The effects of electrostatic, long-range interactions were accounted for by the Ewald summation method. The non-coulombic part was truncated at half the box length. Berendsen thermostat, with a time constant $\tau_B=200\text{ps}$, was used to maintain the desired temperature for the production run. The Verlet algorithm with a time step of 2 fs was used to integrate the equations of motion. The quaternion algorithm was used to maintain the rigid body constraints on the methanol molecules.

The system was studied along two isochores, 0.768 g cm^{-3} and 0.878 g cm^{-3} . The experimental density at 300 K and 1atm is 0.768 g cm^{-3} [25] while 0.878 g cm^{-3} is the density around which the glass transition was reported to occur at around 155 K using the H1 potential [33]. The temperatures studied were 300, 250, 210, 180, 170 and 155 K for the 0.768 g cm^{-3} isochore and 300, 250, 210, 180 and 170 K for the 0.878 g cm^{-3} isochore. The initial configuration for the molecular dynamics simulations at 300 K was generated using the PACKMOL program [34]. The system was then slowly cooled to obtain lower temperatures. The system was equilibrated for 1-4 ns for the temperature range of 300-155K, and the production run lengths were kept between 2-8 ns. The details of run lengths are summarised in Table II. Self-diffusivities were computed using the Einstein relation [35]. Long run lengths were used, particularly at low temperatures, to ensure adequate sampling of configuration space, as measured by the mean squared displacement (MSD) of oxygen atoms, as shown in Figure 1. The time of onset of the diffusional regime, t_{diff} , was identified from the MSD versus time plots as the regime in which the Einstein relation is obeyed. Along an isochore, as the temperature is decreased we observe that the onset of diffusional regime shifts to higher and higher times (0.5 to 2.5 ns). At 155 K, for the 0.768 g cm^{-3} isochore, no linear dependence of the MSD on time is observed even upto 8 ns run length, suggesting that the system is out of equilibrium and we are dealing with an arrested structure. Table II shows the time of onset of diffusional regime, t_{diff} , as determined from the applicability of the Einstein relation to describe the time dependence of the MSDs. Our simulation results are in agreement with previous results [25, 33] within the statistical error bars.

2.3 Generating Power Spectra

Based on our previous work on water where we considered various tagged particle observables, such as local orientational order metrics and tagged particle potential and kinetic energies, we concluded that the tagged particle potential energy is sensitive to a wide range of time scales associated with the hydrogen-bonded network [19]. Therefore, in this study, we focus on the static distributions and power spectra associated with tagged molecule potential energies, $S_u(f)$. The tagged molecule potential energy, $u(t)$, corresponds to the interaction energy of an individual molecule with all the other molecules in the system. Since the configurational potential energy function is pair-additive, the total potential energy, $U(t) = 0.5 \sum_i u_i(t)$ where the sum extends over all molecules.

The tagged particle potential energies were stored at intervals of 10 fs i.e. every 10 MD steps, which corresponds to a Nyquist frequency of 1666 cm^{-1} . The value of the Berendsen thermostat time constant (τ_B) provides the lower limit on the frequency range over which we can obtain reliable power spectra; thus, $\tau_B=200 \text{ ps}$ corresponds to a lower frequency limit of 0.165 cm^{-1} . Standard fast Fourier transform routines were used with a square sampling window. The normalization convention was chosen such that the integrated area under the $S(f)$ curve equalled the mean square amplitude of the time signal. Windows containing 2^{16} data points were used for Fourier transformation [36]. Statistical noise in the power spectra was reduced by averaging overlapping time signal windows as well as individual tagged molecule spectra [18].

Our analysis of the power spectra associated with tagged molecule potential energy focuses on the three distinct regions of the spectrum: (i) identification of resonances or power spectral peaks, typically corresponding to high-frequency local vibrational modes which are weakly coupled to network reorganizations; (ii) identifying the frequency range and the exponent associated with the $1/f^\alpha$ multiple time scale regime, and (iii) the frequency of crossover to white noise behaviour. A linear least-square fitting of $\ln S(f)$ was used to obtain the scaling exponent α associated with the multiple time-scale region.

2.4 Model-based fitting procedure for power-law-like spectra

A procedure for quantitatively fitting the entire power spectrum, and not just the multiple time scale regime, to a physically motivated parametric model for the time-scale distribution associated with molecular motions in water has been developed previously[22]. In this paper, we apply a similar procedure to quantify the temperature-dependent changes that take place along the 0.768 and 0.878 g cm^{-3} isochore of H1 model of liquid methanol. The analytical model is a sum of six functions that correspond to well-defined model behaviors:

- a $S_\beta(f; a, \beta) = a^2/f^\alpha$ power-law noise term containing two parameters, corresponding to the amplitude and spectral index;
- five resonance distributions. Here we have taken a flat distribution of resonance frequencies lying between f_{min} and f_{max} with fixed relaxation rate λ . The resulting spectral densities are

$$S_{res}(f; a, f_{min}, f_{max}, \lambda) = a^2 \int_{f_{min}}^{f_{max}} [\lambda^2 + 4\pi^2(f - f_0)^2]^{-1} df_0. \quad (3)$$

For each resonance, four parameters, corresponding to the amplitude, minimum and maximum resonance frequencies and relaxation rate, must be introduced.

In addition the model function also contains a white noise term and a filter function

$$F(f; \lambda, n) = \frac{1}{((2\pi f/\lambda)^{2n} + 1)} \quad (4)$$

with $n \approx 5$. The filter function takes into account the steep fall off in the spectral density at high frequency, presumably due to the upper limit imposed by the time step of the molecular dynamics algorithm. The filter function is approximated rather roughly by the function $F(f; \lambda, 5)$, the numerical tests show that that the fit is rather insensitive to its exact shape. The overall 24-parameter model is given by:

$$S_{model}(f) = F(f; \lambda_0, 5) \left[S_\beta(f; a_1, \beta_1) + \sum_{k=2}^{k=6} S_{res}(f; a_k, f_{min,k}, f_{max,k}, \lambda_k) \right] + C \quad (5)$$

where C is an additional white noise term.

3 Results and Discussion

3.1 Static distribution of tagged molecule potential energy

Figure 2 shows the static distribution, $P(u)$, of the tagged molecule potential energies, $u(t)$, for methanol at several temperatures along the 0.768 and 0.878 g cm⁻³ isochores. Unlike in the case of monoatomic van der Waals liquids, methanol resembles water and silica in that, it shows multimodal $P(u)$ distributions indicating that there are energetically distinct local environments in the liquid. The presence of distinct peaks suggests that there is a small energetic barrier to transit from one energetic environment to another. This heterogeneity in local environments seems to be characteristic of network-forming liquids, regardless of the dimensionality of the networks. It should be noted that the number of peaks in the $P(u)$ distributions of water and silica are larger but the individual peaks are less distinct.

The three peaks in methanol are centred at approximately at ~ -130 , -85 and -30 kJ mol⁻¹. The distinct demarcation between the three peaks as well as the relative probabilities change with

temperature, with the lowest energy peak becoming less prominent. At low temperatures, just above the glass transition, the relative intensities of the peaks are very sensitive to the quality of equilibration. The mean value of the tagged potential energy, $\langle u \rangle$, varies between -82.4 and -69.2 kJ mol^{-1} between 155 and 300 K along the 0.768 g cm^{-3} isochore. A similar behaviour is observed in case of 0.878 g cm^{-3} isochore. The mean value of the tagged potential energy, $\langle u \rangle$, ranges from -84.17 to -72.3 kJ mol^{-1} between 170 and 300 K along this isochore.

Figure 3 shows the probability distributions corresponding to the tagged molecule potential energy contributions from the van der Waals, screened Coulombic and reciprocal space contributions to the total potential energy for a single state point (300K, 0.768 g cm^{-3}). It is immediately obvious that the multimodal character is due to the electrostatic contribution from the screened Coulombic interactions. The $P(u_{rec})$ and $P(u_{vdW})$ distributions are unimodal and very narrow in comparison with $P(u_{screen})$.

The dependence of the multimodality of the static tagged particle potential energy distribution on the electrostatic contribution was also noted in our previous work on silica [23]. In the Haughney model, the Coulombic contribution is parameterised to take into account the net effect of both hydrogen bonding and multipole moment interactions. To understand the extent to which the peak structure of the $P(u)$ distributions is correlated with the hydrogen bonding, we have classified the methanol molecules based on their tagged particle potential energy into three categories, as defined in Table III, and computed the fraction f_n of n -bonded hydrogen molecules in each category. The geometric criteria for identifying the hydrogen bonds were taken from ref.[25]. Two molecules are regarded to be hydrogen bonded if $r_{OO} \leq 3.5 \text{\AA}$, $r_{OH_O} \leq 2.6 \text{\AA}$ and the angle $\angle H_OOO \leq 30^\circ$. The simulation averages of f_0 , f_1 , f_2 and f_n at 300K and 0.768 g , shown in Table III, reproduce those of Haughney et. al. within statistical error. Activation energies of hydrogen bond lifetimes was found to be 15.6 kJ mol^{-1} , which is close to the previously reported values of 16 kJ mol^{-1} [25, 33].

The results in Table III show that non-bonded molecules are essentially absent in the 170K to 300K regime. The peak centered at -30 kJ mol^{-1} has a somewhat higher value of f_1 and the peak centered at -130 kJ mol^{-1} has a somewhat higher value of f_3 than the overall simulation averaged values of f_1 and f_3 . The CH_3OH molecules which belong to the central peak of the $P(u)$ distribution have an f_n distribution which is essentially identical to the overall ensemble averaged distribution. Therefore the peak structure of the $P(u)$ distributions cannot be attributed to differing degrees of hydrogen bonding, though there is a weak correlation between n_{hb} and u . Our previous work on water, as well as the results in Section 3.4, show that as the electrostatic contribution is turned off and the Lennard-Jones component relatively enhanced, the degree of multimodality diminishes. The multimodality must therefore originate from longer range electrostatic interactions, stretching over at least next nearest

neighbours, in addition to nearest neighbours. It would be interesting, in this context, to study fluids with dipolar, and perhaps higher order multipolar, interactions [35].

3.2 Power spectra of tagged particle potential energy

3.2.1 Comparison of methanol and water

Figure 4 compares the power spectra generated by the fluctuations in the tagged potential energy of methanol, $S_u(f)$, at 300 K and 0.768 g cm^{-3} with that of SPC/E water at 1.0 g cm^{-3} at 300 K. The densities correspond to those observed under ambient temperature and pressure conditions. Despite the difference in the dimensionality of the hydrogen bonded network between methanol and water, the key power spectral features show strikingly similar qualitative features with: (i) high frequency localised modes (ii) a $1/f^\alpha$ multiple time scale regime with exponent α at intermediate frequencies and (iii) a crossover to white noise at low frequencies. The high-frequency cutoff of the power spectrum is determined by the time step used in the molecular dynamics simulations.

Given the rigid molecule approximation used in the present simulations, no intramolecular vibrational modes can be observed in our studies. We briefly summarise the information on specific intermolecular vibrational modes available from previous experimental and simulation studies. In the case of water, there is a broad librational band between 500 and 800 cm^{-1} , as well as two-molecule O-O stretching and three-molecule O-O-O bends at approximately 200 cm^{-1} and 60 cm^{-1} [37, 38, 39]. In the case of methanol, experimental IR spectra locate peaks at approximately 680, 270, 135 and 65 cm^{-1} [28, 40, 41]. The hindered rotations of the methanol molecule, with the methyl group treated as a united atom in the OPLS model [12], are associated with frequencies of approximately 580, 210 and 50 cm^{-1} [42]. Explicit treatment of the geometry of the methyl group in the H1 potential shows that the 270 cm^{-1} peak is associated with the velocity autocorrelation function of the hydroxyl hydrogen atom [25]. More recent studies of the optical spectra of methanol identify the COH pure librational peak as lying between 200 and 300 cm^{-1} and the peak at approximately 600 cm^{-1} as the H-bond constrained libration around the CO bond [43, 44]. The low frequency librational bands at 65 and 135 cm^{-1} are expected to be strongly coupled with intermolecular vibrational modes.

The $S_u(f)$ spectrum of water shows a broad librational band between 500 and 800 cm^{-1} but the intermolecular stretches are not observable at this density and temperature since they lie in the multiple time-scale (MTS) region. In the case of methanol, the two high frequency librational bands are observed as distinct peaks at 270 and 600 cm^{-1} . Lower frequency vibrational bands at 65 and 135 cm^{-1} are not visible as distinct peaks in the $S_u(f)$ spectrum of CH_3OH at this state point because they lie in the MTS region.

The multiple-time scale (MTS) regime in methanol at 300 K and 0.768 g cm^{-3} extends from 0.2 to 200 cm^{-1} . There is, however, a small but distinct change in the exponent α at 40 cm^{-1} ; the α value for 0.2-40 cm^{-1} range is 1.36 while for 40-200 cm^{-1} it is 1.22. For SPC/E water at 300 K and 1.0 g cm^{-3} , the $1/f^\alpha$ region extends from 1-200 cm^{-1} with $\alpha = 1.4$. The presence of a larger number of high-frequency resonances in methanol, compared to water, maybe responsible for this change in the exponent of the MTS regime at approximately 40 cm^{-1} . In the remainder of this paper, we refer as the MTS regime to the frequency interval lying below 40 cm^{-1} and above the frequency of crossover to white noise.

At the equilibrium densities associated with 1 atm pressure and 300K, the white noise regime in water occurs below 1 cm^{-1} whereas for methanol, it begins at a lower frequency of 0.2 cm^{-1} . This suggests that the time taken for the potential energy fluctuations to decorrelate is smaller for water than methanol and therefore the overall relaxation dynamics over length scales of a few molecules will be faster in water than in methanol. This is consistent with the viewpoint expressed by Ladanyi and Skaf [1], based on orientational correlation functions, angular VACFs and NMR relaxation rates, that water and methanol relax at similar scales at short times but the relaxation of CH_3OH becomes much slower for times greater than 0.6ps (55.5 cm^{-1}). The overall faster dynamics of water, despite the existence of a stronger hydrogen bond and an extended three-dimensional network is attributed to the higher translational diffusity due to lighter mass, more rapid librational modes and the coincidence of the direction of the molecular dipole moment with one of the principal axes of rotation [1].

The power spectra associated with the fluctuations in the total tagged potential energy and the contributions from reciprocal and screened energies arising out of Ewald summation and the van der Waals interactions were computed at 300K and 0.768 g cm^{-3} . Though the figure is not shown, the behaviour of $S_u(f)$ is almost exactly reproduced over much of the frequency range by the screened charge contribution. The spectral power associated with the reciprocal space and van der Waals contributions is lower and, therefore has a minor effect on the overall spectrum except in the high-frequency region. The u_{vdW} contribution produces a relatively unstructured power spectrum, more like Argon, while the Coulombic interactions are responsible for much of the high-frequency, short-length scale structure. This is consistent with our earlier observations on silica [23].

3.2.2 Temperature and Density Dependence

The temperature dependence of the power spectra associated with tagged molecule potential energies is considered in Figure 5. Figures 5(a) and 5(b) show $S_u(f)$ curves for different temperatures along the 0.768 and 0.878 g cm^{-3} isochores respectively. The glass transition, as reflected in the time-dependence of the mean-square displacement plots, occurs at a lower temperature for the higher density isochore.

The $S_u(f)$ plots for both densities at 300 K show well-defined librational peaks. As discussed in section 3.2.1, the $1/f^\alpha$ MTS region can be partitioned into a low-frequency MTS regime extending from 0.2-40 cm^{-1} with $\alpha_u = 1.36$ and a higher frequency MTS regime from 40-200 cm^{-1} with exponent 1.22.

At this temperature, there are no peaks lying between 40 and 200 cm^{-1} though molecular centre-of-mass VACFs, far-IR and dielectric loss spectra suggest that vibrational modes at 65 and 135 cm^{-1} corresponding to intermolecular vibrational modes involving two or three molecules should be present. The change in the value of α at approximately 40 cm^{-1} suggests that these two- or three- molecule network modes are partially decoupled from the longer length scale, lower frequency network rearrangements. This discontinuity becomes more pronounced with the lowering of temperature and distinct peaks at approximately 65 and 140 cm^{-1} can be seen in $S_u(f)$ plots at 170 and 155K. These peaks must correspond to caging vibrations of methanol molecules as the system dynamics slows down. For these low temperature isotherms, the onset of diffusional dynamics in the MSD plots is very slow indicating that the system is very close to glass transition. The crossover to white noise which is visible below 0.2 cm^{-1} for the 300K isotherm moves to frequencies below 0.1 cm^{-1} for temperatures of 250K or less. In this study, we did not attempt to generate power spectra at lower frequency since this would have implied using very large values for the time constant of the Berendsen thermostat and therefore would have compromised the temperature control.

3.3 Parametric fitting of the Power Spectra

The results of the fitting of the power spectra along the 0.768 g cm^{-3} isochore is shown in Figure 6. The quality of the fits, given the complex shape of the power spectrum, is good. It is interesting to compare the parametric distribution functions used for water [22] and methanol. Fitting the water power spectra requires only two resonances [22] while fitting the methanol power spectrum requires five resonance terms. In the case of both water and methanol, power spectra were computed over the 0.1 to 1666 cm^{-1} regime. The low frequency white noise is more pronounced for water in this frequency regime than for methanol for the temperatures and densities studied here. As a consequence, a Debye term corresponding to fixed frequency relaxation processes is required for the water spectral fits. In the case of methanol, an additional white noise term and a filter function is used in the fits but no Debye relation term was required.

3.4 Modifying the Strength of Hydrogen Bonding

The H1-model of methanol effectively condenses the information about the short-range repulsion and dispersion using the Lennard-Jones terms. The long- range electrostatic interactions and anisotropic

hydrogen bonding interactions are controlled by the partial charge distribution over the atoms. To study the effect of varying the strength of hydrogen bonding on the power spectra and the static distribution of tagged particle potential energies at 300 K and 0.768 g cm⁻³, we have scaled the H1-model charges. Figure 7 compares the $S_u(f)$ spectra of methanol with normal charges on C, H_O and O with the power spectra when the charges are up-scaled and down-scaled by 10%, at 300 K and 0.768 g cm⁻³. The crossover to white-noise occurs at around 0.2 cm⁻¹ for the system with standard H1 model charges. When the charges are increased by 10%, we see that the librational peak becomes more pronounced and the crossover to white noise shifts to lower frequencies (not shown in the frequency range studied) owing to the fact that now the interactions are much stronger and so is the hydrogen bonded network resulting in a long range correlation between the network dynamics and the local librations in the system. An increase in the extent of multimodality in the probability distribution of static tagged potential energy is also observed with the increase in charges on H1 model of methanol. On the other hand, reduction of the charges by 10%, converts a sharp librational peak occurring in tagged potential energy power spectrum to almost a shoulder and induces a crossover to white noise at frequencies below 1 cm⁻¹. There also occurs a deconstructuring or loss of multimodality in $P(u)$ consistent with the weakening of the hydrogen-bonded network in liquid methanol. As the charges are reduced and the system approaches a Lennard-Jones fluid in its behaviour, the tagged molecule potential energy distribution narrows significantly indicating that the heterogeneity in local molecular environments responsible for multiple time-scale behaviour is lost.

3.5 Connection between multiple time scale behaviour and diffusivity

The self-diffusivity was computed using the Einstein relation from the MSD plots for the oxygen atoms (see Section 2.2). Figure 8 shows the Arrhenius plot of the diffusivity. The activation energies along the 0.768 and 0.878 g cm⁻³ isochores are 10.5 and 14.5 kJ mol⁻¹ respectively. Haughney et al report an activation energy of 13 kJ mol⁻¹ for 0.768 g cm⁻³ isochore; the discrepancy with our values may be due to the fact that our run lengths are more than two orders of magnitude longer.

In simple liquids, diffusion occurs as a combination of collisional and cage relaxation processes. An additional mechanism of diffusion exists in network-forming liquids due to the coupling of local high-frequency modes (e.g. librations in the case of H₂O) with local, two-molecule network re-organizations. As librational modes are more strongly coupled with network-reorganizations, the exponent α rises as does the diffusivity, leading to a strong positive correlation between D and α_u , as discussed in our earlier work on water and silica [20, 23]. Figure 9 demonstrates that this relationship between α_u and the diffusivity also holds in methanol. Clearly, the librational coupling to larger scale H-bonded network reorganisations is an important diffusional mechanism in CH₃OH, as in water and silica,

despite the differences in network dimensionality. It should be noted that we have computed α_u values by fitting $\ln S_u(f)$ over the 1 to 40 cm^{-1} regime which is expected to be particularly sensitive to the coupling of the two- and three-molecule modes with the network regorganisations.

In order to make a quantitative comparison of the correlation between diffusivity and the scaling exponent, Figure 10 plots a dimensionless diffusivity, D^* , against α_u for CH_3OH , H_2O and SiO_2 in the liquid phase. The dimensionless diffusivity, D^* , is defined as $D^* = D\rho^{1/3}/\sqrt{k_B T/m}$ where ρ and m correspond to the number density and molecular mass of the formula units (H_2O , SiO_2 and CH_3OH). The correlation is very similar in all three cases, though given the differences in intermolecular interactions, some scatter in the correlation plot is expected. Typically, as temperatures and densities increase and the network structure breaks down, the α values become less sensitive to the diffusivity; in the limiting case of a simple liquid, α_u is zero and uncorrelated with the diffusivity.

4 Conclusions

In this work, we have focused on understanding the structure and dynamics of liquid methanol by studying the static distributions and temporal correlations associated with fluctuations in the tagged molecule potential energies. While the tagged molecule potential energy is not a directly accessible quantity, previous work on water, aqueous alkali halide solutions and silica melt have demonstrated that this quantity is sensitive to network reorganisations on several time scales. In the case of methanol, we show that analysis of this single, frequency-dependent power spectral distribution provides an overall view of the dynamics, including important resonances and the multiple time-scale regime associated with network formation. This is particularly interesting given that the resonances at 650 cm^{-1} , 270 cm^{-1} , 135 cm^{-1} and 65 cm^{-1} have otherwise been identified using very different correlation functions corresponding to different experimental techniques.

The static distribution of tagged molecule potential energies shows a clear multimodal structure with three distinct peaks. Similar multimodal distributions were observed earlier in the case of water and silica melt at low temperatures and densities. For both the systems, factors which attenuate the network, such as temperature, density and or ionic solutes, were found to destroy the multimodal character and lead to unimodal Gaussian-type distributions characteristic of simple liquids. In the case of methanol, we have further found that the correlation between number of hydrogen bonds, as identified by geometric criteria, and the tagged particle potential energy is very weak. The multimodality seems to therefore be due to electrostatic effects, but not necessarily due to local anisotropic interactions. The longer range of electrostatic interactions, such as dipole-dipole interactions, presumably implies that the organisation of second and third neighbour shells plays a crucial role in determining the tagged

particle potential energy distributions. In this context, it would therefore be interesting to examine strongly dipolar, but not necessarily hydrogen-bonded systems.

An interesting outcome of this study is the remarkable similarity in the tagged potential energy power spectra of methanol, water and silica, despite the differences in the underlying interactions and the dimensionality of the network. All three liquids show a distinct multiple time scale (MTS) regime with a $1/f^\alpha$ dependence with a clear positive correlation between the scaling exponent α and the diffusivity. The low-frequency limit of the MTS regime is determined by the frequency of crossover to white noise behaviour which occurs at approximately 0.1 cm^{-1} in the case of methanol under standard temperature and pressure conditions. The power spectral regime above 200 cm^{-1} in all three systems is dominated by resonances due to localised vibrations, such as librations. The correlation between α and the diffusivity in all three liquids appears to be related to the strength of the coupling between the localised motions and the larger length/time-scale network re-organizations. Thus the time scales associated with network reorganization dynamics do not appear to be qualitatively different in these systems, despite the fact that water and silica both display diffusional anomalies but methanol does not. This suggests that the equilibrium transport properties associated with the anomalies may be more sensitive to the way a liquids samples the overall configuration space, i.e. the excess entropy scaling of transport properties, than the short time dynamics. Given that time-resolved infra-red techniques have been used to monitor the hydrogen-bond dynamics in water, it would be interesting to compare the solvation dynamics in water with that in methanol and other low-molecular weight alcohols.

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References

- [1] Ladanyi, B. M.; Skaf M.S. *Ann. Rev. Phys. Chem.* **1993**, *44*, 335.
- [2] Bagchi, B. *Ann. Rev. Phys. Chem.* **2003**, *99*, 127.
- [3] Bagchi, B. *Chem. Rev.* **2005**, *105*, 3197.
- [4] *Hydration Processes in Biology* edited by Bellissent-Funel, M.-C. (IOS Press, Amsterdam, 1999)
- [5] Loparo, J. L.; Roberts, S. T.; Tokmakoff, A. *J. Chem. Phys.* **2006**, *125*, 194521.
- [6] Loparo, J. L.; Roberts, S. T.; Tokmakoff, A. *J. Chem. Phys.* **2006**, *125*, 194522.

- [7] Rezus, Y. L. A.; Bakker, H. J. *J. Chem. Phys.* **2005**, *123*, 114502.
- [8] Raiteri, P.; Laio, A.; Parrinello, M. *Phys. Rev. Lett.* **2004**, *93*, 087801.
- [9] Luzar, A.; Chandler, D. *Phys. Rev. Lett.* **1996**, *76*, 928.
- [10] Tokmakoff, A. *Science* **2007**, *317*, 54.
- [11] Texeira, J. in *Hydration Processes in Biology* edited by Bellissent-Funel, M.-C. (IOS Press, Amsterdam, 1999)
- [12] Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.
- [13] Yamaguchi, T.; Hidaka, K.; Soper, A. K. *Mol. Phys.* **1999**, *96*, 1199.; erratum *Mol. Phys.* **1999**, *97*, 603.
- [14] Yamaguchi, T.; Benmore, C. J.; Soper, A.K. *J. Chem. Phys.* **2000**, *112*, 8976.
- [15] Weitkamp, T.; Neufeind, J.; Fischer, H. E.; Zeidler, M. D. *Mol. Phys.* **2000**, *98*, 125.
- [16] Madden, P. A. and Wilson, M. *J. Phys.: Condensed Matter* **12**, A95, 2000.
- [17] Wang, M. C.; Uhlenbeck, G. E. *Rev. Mod. Phys.* **1945** *17*, 323.
- [18] Mudi, A.; Ramaswamy, R.; Chakravarty, C. *Chem. Phys. Lett.* **2003**, *376*, 683.
- [19] Mudi, A.; Chakravarty, C. *J. Phys. Chem. B* **2004**, *108*, 19607.
- [20] Mudi, A.; Chakravarty, C. *J. Chem. Phys.* **2005**, *122*, 104507.
- [21] Mudi, A.; Chakravarty, C. *J. Phys. Chem. B* **2006**, *110*, 8422.
- [22] Mudi, A.; Chakravarty, C.; Milotti, E. *J. Chem. Phys.* **2006**, *125*, 074508.
- [23] Sharma, R.; Mudi, A.; Chakravarty, C. *J. Chem. Phys.* **2006**, *125*, 044705.
- [24] Sasai, M.; Ohmine, I.; Ramaswamy, R. *J. Chem. Phys.* **1992**, *96*, 3045.
- [25] Haughney, M.; Ferrario M.; McDonald, I. R. *J. Phys. Chem.* **1987**, *91*, 4934.
- [26] Wallen, S.L.; Palmer, B.J.; Garrett, B. C.; Yonker, C. R. *J. Phys. Chem.* **1996**, *100*, 3959.
- [27] Asahi, N.; Nakamura, Y. *J. Chem. Phys.* **1998**, *109*, 9879.
- [28] Venables, D. S.; Chiu, A.; Schmuttenmaer C. A. *J. Chem. Phys.* **2000**, *113*, 3243.

- [29] Tsuchida, E.; Kanada, Y.; Tsukada, M. *Chem. Phys. Lett.* **1999**, *311*, 236.
- [30] Handgraaf, J-W.; Meijer, E. J.; Gaigeot, M-P. *J. Chem. Phys.* **2004**, *121*, 10111.
- [31] Smith, W.; Forester, T. R. *J. Mol. Graphics* **1996**, *14*, 136.
- [32] Smith, W.; Yong, C. W.; and Rodger, P. M. *Mol. Simulat.* **2002**, *28*, 385.; The DL_POLY website is http://www.cse.clrc.ac.uk/msi/software/DL_POLY/.
- [33] Sindzingre, P.; Klein, M. L. *J. Chem. Phys.* **1992**, *96*, 4681.
- [34] Martinez, J. M.; Martinez, L. *J. Comp. Phys.* **2003**, *24* (819).
- [35] Hansen, J.-P.; McDonald, I. R.; *Theory of Simple Liquids* (Academic Press, 1986).
- [36] Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. : *Numerical Recipes in Fortran* (Cambridge University Press, Cambridge, 1990).
- [37] Madden, P. A.; Impey, R. W. *Chem. Phys. Lett.* **123**, *502*, 1986.
- [38] Guillot, B. *J. Chem. Phys.* **95**, *1543*, 1991.
- [39] Parker, M. E.; Heyes, D. M. *J. Chem. Phys.* **108**, *9039*, 1998.
- [40] Passchier, W. F.; Klompmaker, E. R.; Mandel, M. *Chem. Phys. Lett.* **1970**, *4*, 485.
- [41] Guillot, B.; Marteau, P.; Obriot, J. *J. Chem. Phys.* **1990**, *93*, 6148.
- [42] Matsumoto, M; Gubbins, K. E. *J. Chem. Phys.* **93**, *1981*, 1990.
- [43] Chelli, R.; Ciabatti, S.; Cardini, G., Righini, R.; Procacci, P. *J. Chem. Phys.* **1999**, *111*, 4218.
- [44] Pagliai, M.; Cardini, G., Righini, R.; Schettino V. *J. Chem. Phys.* **2003**, *119*, 6655.

Table I

Potential Parameters of Haughney's H1 model

Atom	ϵ (kJ/mol)	$\sigma(\text{\AA})$	$q(\text{e})$
C	0.7576	3.861	0.297
O	0.7309	3.083	-0.728
H_O			0.431

Table II

Summary of Computational Details for MD simulations of H1 methanol. The lengths of equilibration and production runs are denoted by t_{eq} and t_{prod} respectively. The time of onset of the diffusional regime is denoted by t_{diff} .

Temperature (K)	0.768 g cm ⁻³			0.878 g cm ⁻³		
	t_{eq} (ns)	t_{prod} (ns)	t_{diff} (ns)	t_{eq} (ns)	t_{prod} (ns)	t_{diff} (ns)
300	1	2	0.05	1	2	0.05
250	1	2	0.08	1	2	0.10
210	2	4	0.20	2	4	0.40
180	3	6	2.00	3	6	3.00
170	3	6	2.50	3	6	3.00

Table III

Hydrogen bond statistics of methanol molecules at two different state points. The fraction of molecules with n hydrogen-bonded neighbours is denoted by f_n , The ensemble averaged values of f_n are cocomputed, in addition to the averages over molecules belong to restricted ranges in the tagged molecule potential energy, u .

300 K, 0.768 g cm ⁻³					
u (kJ mol ⁻¹)	$\langle n_{hb} \rangle$	f_0	f_1	f_2	f_3
$u \geq -48$	1.68	0	0.28	0.63	0.05
$-48 < u \geq -103$	1.87	0	0.19	0.72	0.08
$u < -103$	2.12	0	0.04	0.80	0.16
ensemble average	1.86	0.017	0.19	0.71	0.082

170 K, 0.768 g cm ⁻³					
u (kJ mol ⁻¹)	$\langle n_{hb} \rangle$	f_0	f_1	f_2	f_3
$u \geq -54$	1.91	0	0.105	0.88	0
$-54 < u \geq -108$	1.98	0	0.05	0.92	0.028
$u < -108$	2.07	0	0.0056	0.92	0.07
ensemble average	1.99	0.00013	0.04	0.92	0.037

Figure Captions

1. Mean square displacements (MSDs) for different temperatures along (a) 0.768 g cm^{-3} and (b) 0.878 g cm^{-3} isochores. Note the logarithmic scale along both the axes of the plot.
2. Static distribution, $P(u)$, of tagged potential energy, u , of methanol, along (a) 0.768 g cm^{-3} and (b) 0.878 g cm^{-3} isochores at different temperatures.
3. Contributions of reciprocal space, screened Coulomb and van der Waals interactions to the static distribution of tagged particle potential energy of methanol at 300 K and 0.768 g cm^{-3} . $P(u_{rec})$ has been scaled by 1/12 while $P(u_{vdw})$ has been scaled by a factor of half.
4. Comparison of power spectra associated with temporal fluctuations in tagged particle potential energy, $S_u(f)$, between methanol (H1 potential) and water (SPC/E potential) at 300K. The densities of methanol and water were taken as 0.768 g cm^{-3} and 1 g cm^{-3} , corresponding to experimental densities at 1 atmosphere pressure.
5. Power spectra of tagged particle potential energy fluctuations, $S_u(f)$, of methanol, at different temperatures along (a) 0.768 g cm^{-3} and (b) 0.878 g cm^{-3} isochores. Relative magnitudes of power spectra for different temperatures were scaled for clarity of presentation.
6. Power spectra of tagged potential energy, $S_u(f)$ of methanol fitted using the parameteric model defined in Section 2.3 along the 0.768 g cm^{-3} isochore at (a) 300K and (b) 155 K. The raw power spectral data are shown with points and the overall fit is shown in solid lines.
7. Effect of modifying the partial charge distribution of the H1 model potential on: (a) Power spectra of fluctuations of tagged particle potential energies, $S_u(f)$; (b) Static distributions of tagged particle potential energies at 300 K and 0.768 g cm^{-3} . Relative magnitudes of power spectra, $S_u(f)$, are scaled for clarity.
8. Arrhenius plot of self diffusion coefficient of oxygen along 0.768 and 0.878 g cm^{-3} isochores.
9. Correlation plot between the self-diffusion coefficient of oxygen and the scaling exponent, α_u of the multiple time-scale region of the $S_u(f)$ power spectra in methanol. Diffusivities are in units of $\text{cm}^2 \text{ sec}^{-1}$.
10. Correlation plot between the self-diffusion coefficient of oxygen in methanol and water, and silicon ion in silica with the scaling exponent, α_u of the multiple time-scale region of the $S_u(f)$ power spectra. Dimensionless diffusivities, $D^* = D\rho^{1/3}/\sqrt{k_B T/m}$ where ρ and m correspond to the

number density and masses of the formula units have been used to facilitate comparison between the different systems.

Figure 1:

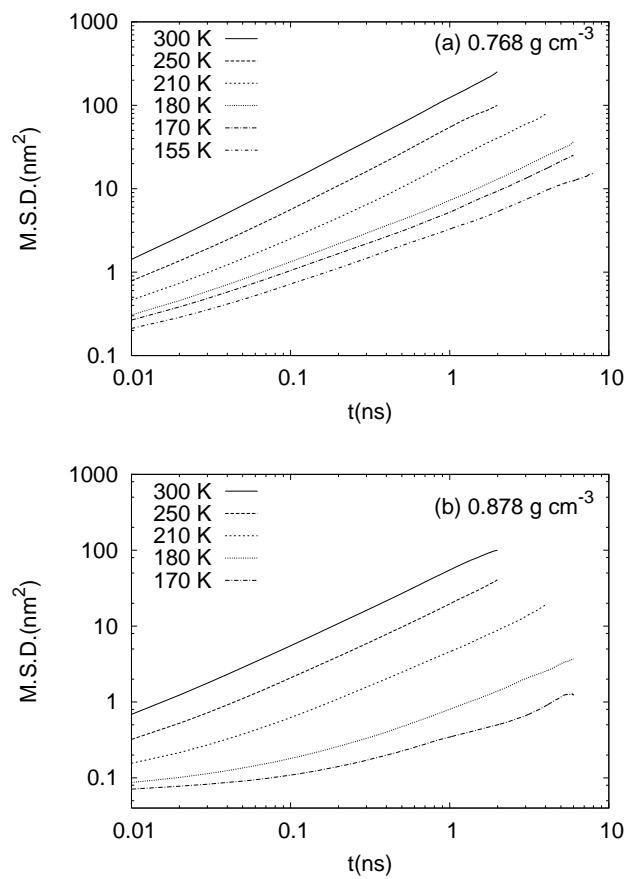


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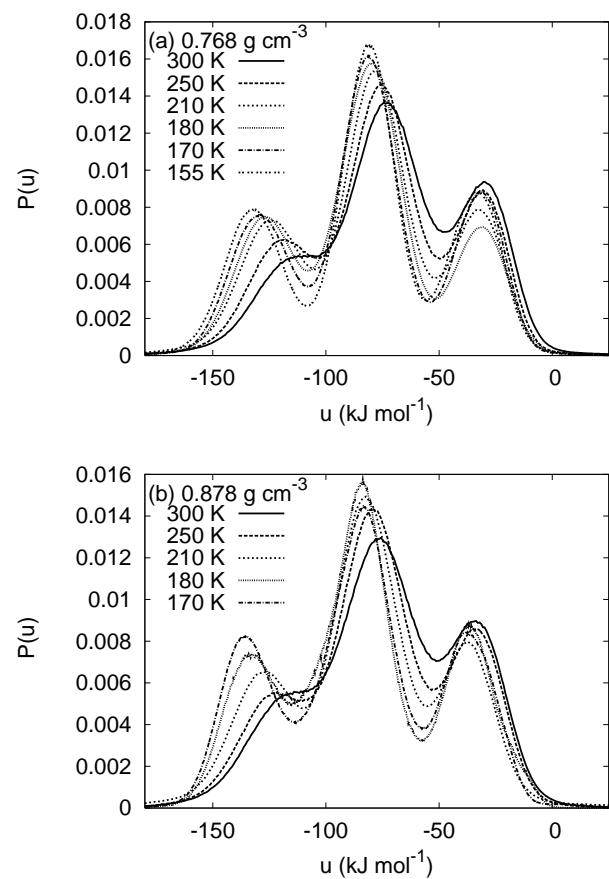
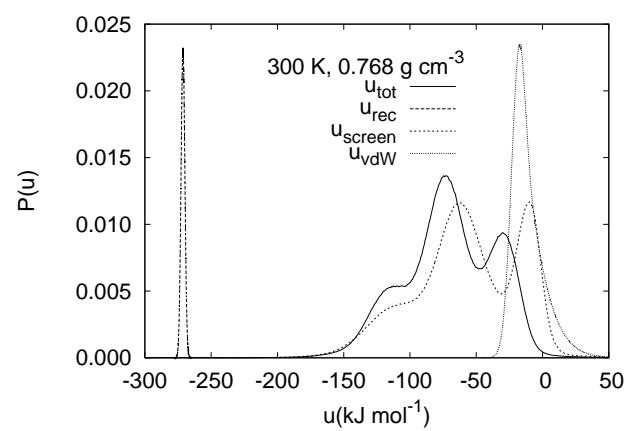
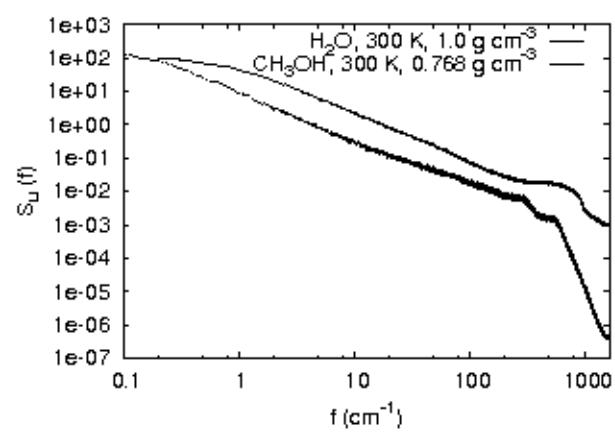


Figure 3:





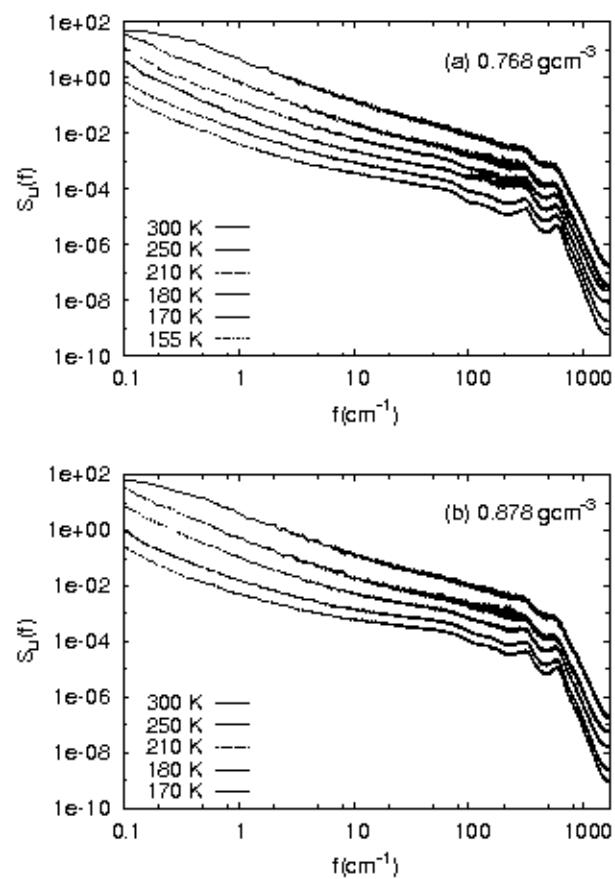
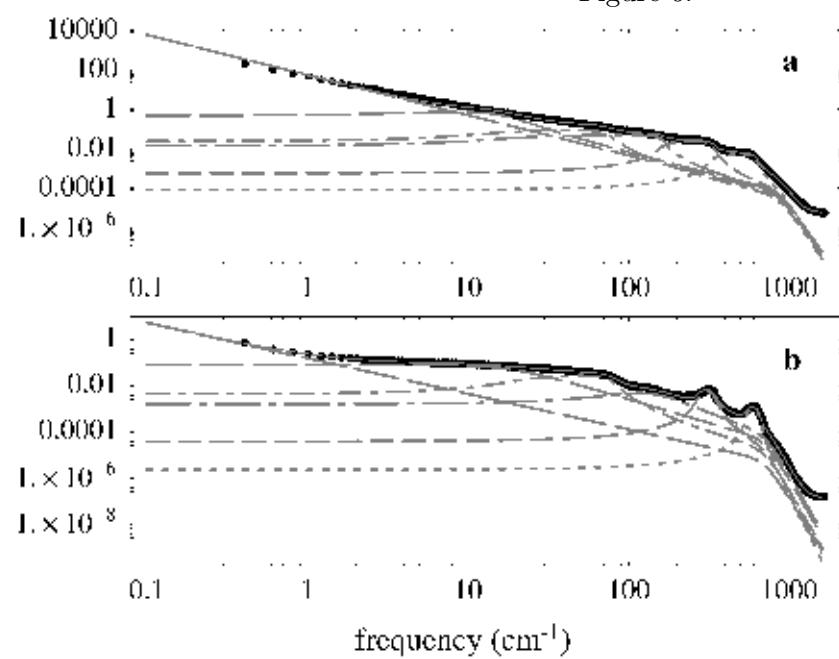


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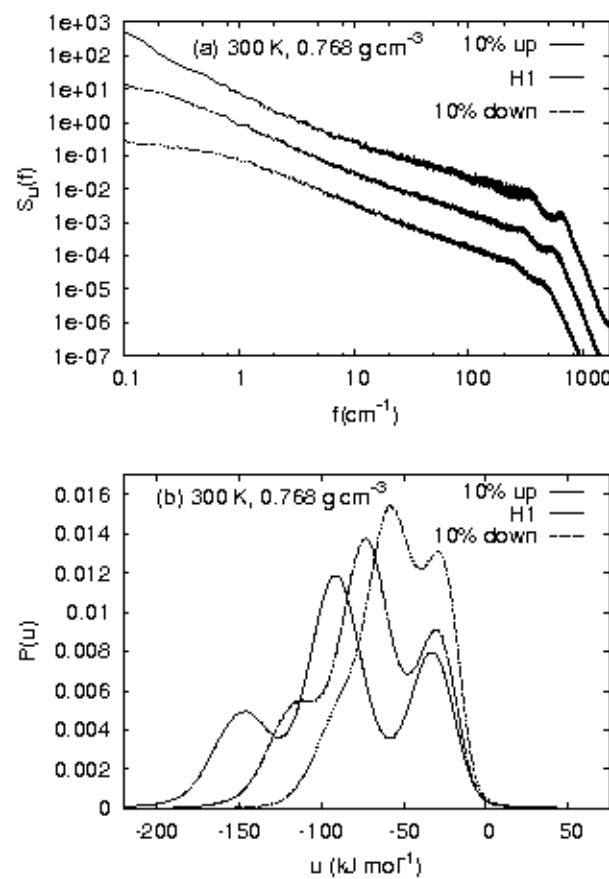


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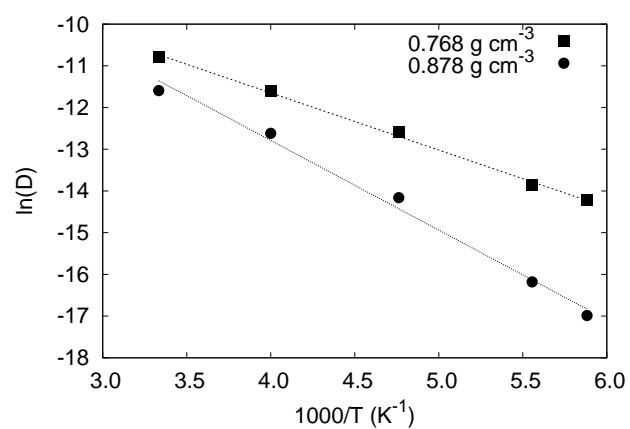


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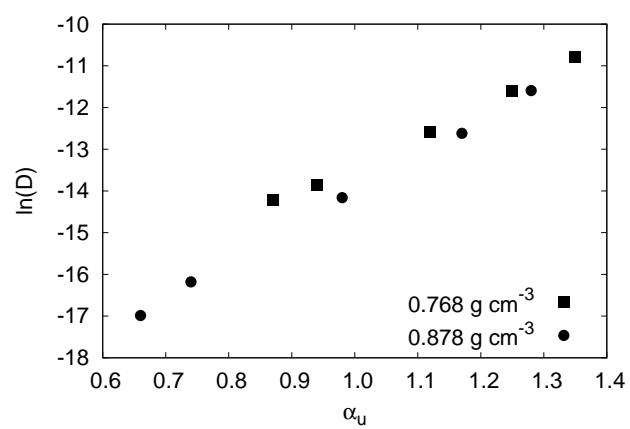


Figure 10:

